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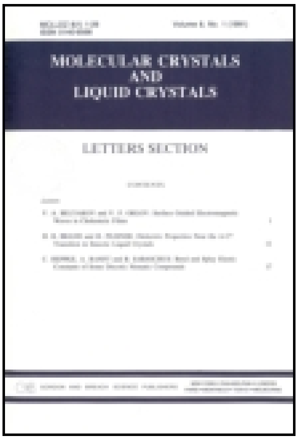

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Synthesis and Crystal Structures of trans-2-(2-Methoxyphenyl)-1-nitroethylene and trans-1-Hydroxymethyl-2-(2-methoxyphenyl)-1-nitroethylene Dichloromethane Hemisolvate

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Synthesis and Crystal Structures of *trans*-2-(2-Methoxyphenyl)-1-nitroethylene and *trans*-1-Hydroxymethyl-2-(2-methoxyphenyl)-1-nitroethylene Dichloromethane Hemisolvate

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*Two nitroalkene compounds, namely trans-2-(2-methoxyphenyl)-1-nitroethylene (**1**) and trans-1-hydroxymethyl-2-(2-methoxyphenyl)-1-nitroethylene dichloromethane hemisolvate (**2**), have been synthesized and structurally characterized by elemental analysis, ^1H (^{13}C) NMR spectra, and single-crystal X-ray diffraction. The nitroethylene molecules in (**1**) and (**2**) adopt a trans configuration about the C═C double bonds. The crystal structures of (**1**) and (**2**) are stabilized by the C─H···O short contacts, and particularly for (**2**) intermolecular O–H···O hydrogen bonds are also observed.*

[*Supplemental materials are available for this article. Go to the publisher's online edition of Molecular Crystals and Liquid Crystals to view the free supplemental file:* Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 892535 and 892537 for the title compounds (**1**) and (**2**), respectively. Copies of the data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving. html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.]

Keywords Crystal structures; intermolecular interaction; nitroethylene; synthesis

Introduction

The nitroalkene compounds are generally prepared by an aldol type C─C bond formation process, in specific Henry condensation of carbonyl compounds with a nitroalkane to β-nitroalcohol followed by dehydration [1, 2]. Most particularly, the aromatic nitroalkene compounds have been proved to be a significant class of the nitroalkenes, which possess diverse biological activities such as molluscicidal activities [3, 4], insencticidal activities [4], antimicrobial activities [5, 6], anticancer activities [7], anti-HIV-1 activities [8], and so on. Detailed study on the synthesis and structures of such compounds

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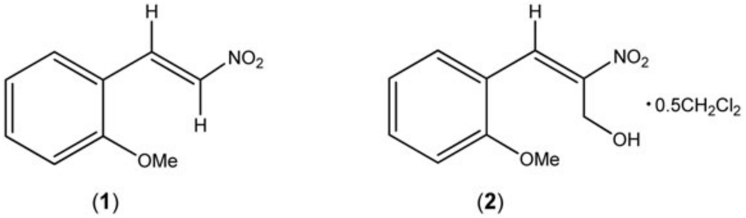


Figure 1. The molecular structures of the title compounds (**1**) and (**2**).

seems very important to better understand the relationship between molecular structures and biological activities. Based on the above information and as a continuation of our studies on such compounds, we herein report that two nitroalkene compounds, *trans*-2-(2-methoxyphenyl)-1-nitroethylene (**1**) and *trans*-1-hydroxymethyl-2-(2-methoxyphenyl)-1-nitroethylene dichloromethane hemisolvate (**2**), have been synthesized and their structures were characterized using the single-crystal X-ray diffraction method as well as spectroscopic techniques. Their molecular structures are shown in Fig. 1. In this context, we now wish to present the detailed crystal structure analyses of the title compounds (**1**) and (**2**) based on X-ray diffraction.

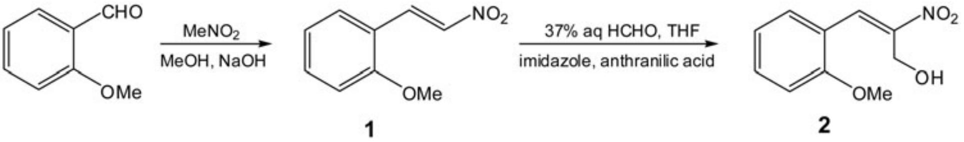
Experimental

Materials and Instruments

All the chemicals were of reagent grade and used without further purification. Melting points were determined on a YRT-3 apparatus and are uncorrected. Elemental analyses for carbon, hydrogen, and nitrogen were performed on a Perkin-Elmer 240C analyzer. ^{1}H (^{13}C) NMR spectra were obtained on a Bruker Avance 400 MHz spectrometer.

Synthetic Procedures

The synthetic route of the title compounds (**1**) and (**2**) is presented in Scheme 1.



Scheme 1. Synthetic route for the title compounds (**1**) and (**2**).

Synthesis of trans-2-(2-Methoxyphenyl)-1-nitroethylene (1)

2-Methoxybenzaladehyde (2.72 g, 20.0 mmol), nitromethane (2.72 mL, 50.0 mmol), and methanol (8.40 mL) are added to a three-neck round bottomed flask and cooled to 0°C. While maintaining the internal reaction temperature between 0°C and 15°C, aqueous 1 M NaOH (50.00 mL, 50.0 mmol) is added by an addition funnel and the mixture is stirred for 15 min. Ice water mixture (35.00 mL) is added and the reaction is stirred at 0°C for

30 min. The reaction mixture is slowly added to aqueous 8 M HCl (33.50 mL, 268.0 mmol) and allowed to stir until the reaction is confirmed complete by TLC. The reaction mixture is filtered and recrystallized from ethanol to give the yellow solid (0.86 g, yield of 24%). Mp: 45°C–46°C. Anal. Calcd. (%) for $C_9H_9NO_3$: C, 60.33, H, 5.06, N, 7.82. Found (%): C, 60.19, H, 5.35, N, 7.65. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ/ppm: 8.18 (d, 1H), 7.89 (d, 1H), 7.46 (m, 2H), 7.00 (m, 2H), 3.96 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS) δ/ppm: 159.5, 138.3, 135.5, 133.5, 132.5, 121.1, 119.2, 111.4, 55.7.

Synthesis of trans-1-Hydroxymethyl-2-(2-methoxyphenyl)-1-nitroethylene Dichloromethane Hemisolvate (2)

To a stirred solution of (**1**) (0.90 g, 5.0 mmol) in THF (10.00 mL) at room temperature was added imidazole (0.34 g, 100 mol%) followed by anthranilic acid (0.07 g, 10 mol%). Formaldehyde (38% aqueous, 10.00 mL) was then added and the reaction mixture was stirred at room temperature. After the completion of the reaction (confirmed by TLC analysis), the reaction mixture was acidified with water (25.00 mL) and the aqueous layer was extracted with EtOAc (3 × 50.00 mL). The combined organic layers were dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was separated by silica gel column chromatography eluting with EtOAc/pet. ether to afford a bright-yellow solid (0.50 g, yield of 48%). Mp: 38°C–39°C. Anal. Calcd. (%) for $C_{10}H_{11}NO_4$: C, 57.41, H, 5.30, N, 6.70. Found (%): C, 57.66, H, 5.54, N, 6.50. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ/ppm: 8.18 (s, 1H), 7.39 (t, 1H), 7.14 (d, 1H), 7.09 (s, 1H), 7.03 (d, 1H), 4.70 (s, 2H), 3.85 (s, 3H), 2.52 (br s, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS) δ/ppm: 158.4, 148.9, 134.0, 132.8, 130.7, 121.0, 120.5, 110.8, 57.1, 55.7.

Single-Crystal X-ray Diffraction

Single crystals of the title compounds (**1**) and (**2**) suitable for X-ray diffraction analyses were grown by slow evaporation of the CH_2Cl_2/hexane solution at 5°C. Two single crystals with dimensions of 0.20 mm × 0.18 mm × 0.12 mm for (**1**) and 0.16 mm × 0.14 mm × 0.12 mm for (**2**) were mounted on a Rigaku Saturn CCD area deterctor. Data were collected at 113(2) K by using a graphite monochromator with Mo$K\alpha$ radiation (λ=0.71073 Å) for (**1**) and Cu$K\alpha$ radiation (λ = 1.54187 Å) for (**2**) in the ω-ϕ scanning mode. Absorption corrections were performed by SADABS program [9]. The structures were solved by direct methods using the SHELXS-97 program [10] and refined by full-matrix least-squares techniques (SHELXL-97) [11] on $F2$. Hydrogen atoms were located using the geometric method. Details of crystal data, data collection, and structure refinement for (**1**) and (**2**) are listed in Table 1. Selected bond lengths and angles for (**1**) and (**2**) are given in Table 2. Hydrogen bonding interactions for (**2**) are summarized in Table 3.

Results and Discussion

Spectral Analyses

The synthesized nitroethylene compounds were characterized by elemental analysis and ^{1}H (^{13}C) NMR spectra. Their structures were unambiguously determined using X-ray diffraction analysis. The elemental analysis and NMR spectra have been in good agreement with the formulae proposed by the X-ray crystallography for (**1**) and (**2**), respectively.

Table 1. Crystal data and structural refinement details for (**1**) and (**2**)

Compounds	(**1**)	(**2**)
Empirical formula	$C_9H_9NO_3$	$C_{21}H_{24}Cl_2N_2O_8$
Formula weight	179.17	503.32
Temperature (K)	113(2)	113(2)
Wavelength (Å)	0.71073	1.54187
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/n	C12/c1
Unit cell dimensions (Å, °)	$a = 5.415(3)$, $b = 16.813(8)$, $c = 9.430(5)$, $\alpha = 90$, $\beta = 99.579(6)$, $\gamma = 90$	$a = 24.450(2)$, $b = 9.7630(9)$, $c = 9.9760(10)$, $\alpha = 90$, $\beta = 96.523(16)$, $\gamma = 90$
Volume (Å^3), Z	846.5(7), 4	2255.4(4), 4
Calculated density (g cm^{-3})	1.406	1.482
Absorption coefficient μ (mm^{-1})	0.107	3.044
F(000)	376	1048
Crystal size (mm^3)	0.20 × 0.18 × 0.12	0.16 × 0.14 × 0.12
θ Range for data collection (°)	2.42–26.02	3.82–72.13
Limiting indices	$-6 <= h <= 6$, $-20 <= k <= 18$, $-11 <= l <= 11$	$-28 <= h <= 30$, $-12 <= k <= 8$, $-12 <= l <= 12$
Reflection collected	7736	10663
Independent reflection	1677 ($R_{int} = 0.0525$)	2192 ($R_{int} = 0.0311$)
Completeness to $\theta_{\max}$ (%)	99.9	98.3
Data/restraints/parameters	1677/0/119	2192/2/158
Goodness of fit on F^2	1.003	1.164
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0347$, $wR_2 = 0.0828$	$R_1 = 0.0582$, $wR_2 = 0.1294$
R indices (all data)	$R_1 = 0.0469$, $wR_2 = 0.0856$	$R_1 = 0.0604$, $wR_2 = 0.1326$
Largest difference peak and hole (e A^{-3})	0.141 and −0.268	0.473 and −0.636
CCDC number	892535	892537

Crystal Structure Description of the Title Compound (1)

As depicted in Fig. 2, the nitroethylene molecule in (**1**) displays a *trans* configuration about the C=C double bond. The bond lengths and angles (Table 2) are in agreement with those observed in the reported similar species [12–22]. The C8=C9 bond length (1.3248(19) Å) is close to the isolated C=C bond (1.337 Å) [12], conforming it is a double bond. The C9—N1 bond length (1.4389(17) Å) and the C8—C7 bond length (1.4525(19) Å) are shorter than the normal C—N single bond (1.472 Å) [12] and the normal C—C single bond (1.46 Å) [23], respectively, mainly due to the strong π-electron delocalization of the molecular

Table 2. Selected bond lengths (Å) and bond angles (°) for (**1**) and (**2**)

Compound (**1**)					
O(2)-N(1)	1.2283(15)	N(1)-C(9)	1.4389(17)	C(7)-C(8)	1.4525(19)
O(3)-N(1)	1.2401(15)	O(1)-C(1)	1.4347(17)	C(8)-C(9)	1.3248(19)
O(2)-N(1)-O(3)	122.70(11)	C(2)-O(1)-C(1)	118.06(10)	C(6)-C(7)-C(8)	122.70(13)
O(2)-N(1)-C(9)	120.61(12)	C(6)-C(7)-C(2)	118.27(12)	C(2)-C(7)-C(8)	118.99(12)
O(3)-N(1)-C(9)	116.69(12)	C(8)-C(9)-N(1)	120.22(13)	C(9)-C(8)-C(7)	125.91(13)
Compound (**2**)					
O(3)-N(1)	1.2369(18)	N(1)-C(8)	1.470(2)	C(2)-C(7)	1.462(2)
O(4)-N(1)	1.2333(18)	O(1)-C(10)	1.440(2)	C(7)-C(8)	1.343(2)
O(4)-N(1)-O(3)	122.96(14)	O(1)-C(1)-C(2)	115.42(14)	C(8)-C(7)-C(2)	125.71(14)
O(4)-N(1)-C(8)	119.62(13)	O(1)-C(1)-C(6)	124.18(15)	C(7)-C(8)-N(1)	117.15(14)
O(3)-N(1)-C(8)	117.42(13)	N(1)-C(8)-C(9)	114.39(13)	C(7)-C(8)-C(9)	128.34(15)

Table 3. Hydrogen bond lengths (Å) and bond angles (°) for (**2**)

D—H···A	d(D—H)	d(H···A)	d(D···A)	∠DHA
O(2)—H(2A)···O(2)[a]	0.83(3)	2.03(3)	2.843(3)	167(4)
O(2)—H(2B)···O(2)[b]	0.84(3)	2.05(3)	2.854(3)	160(4)

Symmetry codes: [a] $-x, -y, -z+1$; [b] $-x, +y, -z+1/2$.

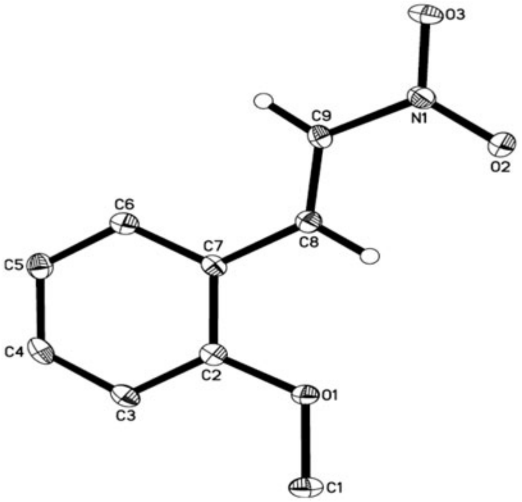


Figure 2. Crystal structure of (**1**) with 30% probability thermal ellipsoids.

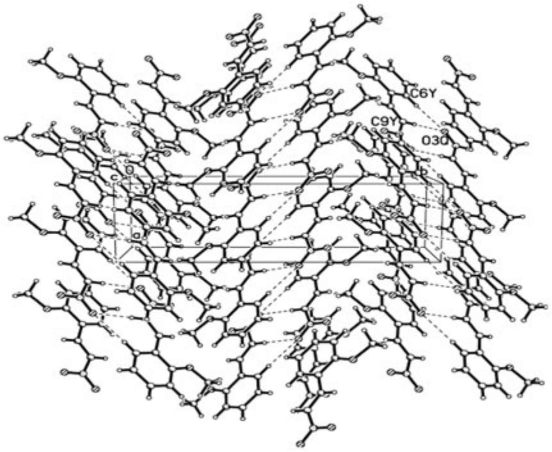


Figure 3. Crystal packing diagram of (**1**) along the *c*-axis.

system [14]. Furthermore, the dihedral angle between the C2—C7 plane (r.m.s. deviation 0.0038 Å) and the N1/O2/O3/C8/C9 plane (r.m.s deviation 0.0132 Å) is 6.1°, suggesting that the nitroethylene moiety is almost coplanar with the *o*-methoxyphenyl moiety. This is because the significant level of π-electron delocalization in the molecular system leads to the planarity of the molecule [14]. In addition, the N1—O3 bond length is about 0.012 Å longer than the N1—O2 bond length, possibly owing to the weak interaction between O atom of the nitro group and the H atom of the phenyl group [12].

As shown in Fig. 3, the crystal packing of (**1**) is stabilized by the C—H···O short contacts involving the H atoms of the phenyl and vinyl groups as well as the O atoms of the nitro group [13, 18]. For example, the O3Q atom from the nitro group has a short nonbonded contact with the H atoms attached to the phenyl C6Y and vinyl C9Y atoms (the distance is 2.530 Å and 2.428 Å, respectively) between the adjacent molecules within a one-dimensional layered network.

Crystal Structure Description of the Title Compound (2)

As depicted in Fig. 4, the nitroethylene molecule in (**2**) adopts a *trans* configuration about the C=C double bond. The bond lengths and angles (Table 2) are within normal ranges, and are comparable to those observed in (**1**). The C7=C8 bond length is 1.343(2) Å, which is a typical double bond and it is longer than that in (**1**). The C8—N1 bond length (1.470(2) Å) and the C7—C2 bond length (1.462(2) Å) are very close to the corresponding normal single bond length [12, 23], which means that the degree of the π-electron delocalization in (**2**) is remarkably weaker than those in (**1**). Furthermore, the dihedral angle between the C1—C6 plane (r.m.s. deviation 0.0096 Å) of the *o*-methoxyphenyl moiety and the N1/O3/O4/C7/C8/C9 plane (r.m.s deviation 0.0137 Å) of the 1-hydroxymethyl-1-nitroethylene moiety is 42.9°, which is sharply larger than the corresponding angle of (**1**). This indicates that the molecule of (**2**) is much less planar compared to that of (**1**), probably because of the steric repulsion and intermolecular interactions of the hydroxymethyl substituent, which is a bigger group with respect to the ethylenic hydrogen atom [22]. In addition, the N1—O3 bond length (1.2369(18) Å) and the N1—O4 bond length (1.2333(18)

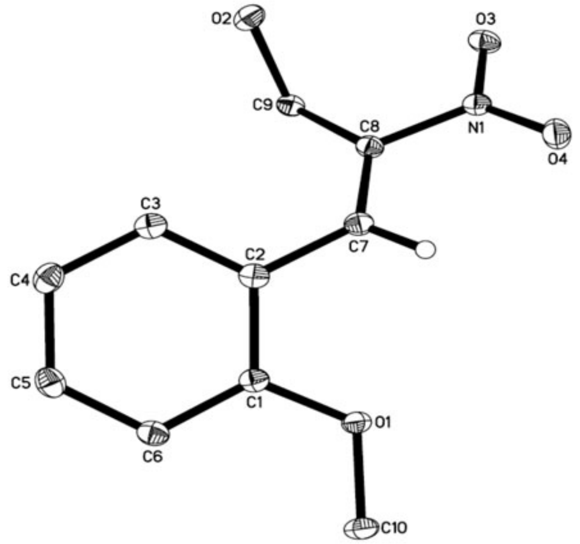


Figure 4. Crystal structure of (**2**) with 30% probability thermal ellipsoids.

Å) in (**2**) are almost identical, which is different from the nonequivalent N—O bond lengths of the nitro group in (**1**).

As shown in Fig. 5, there are some similar C—H···O short contacts like (**1**). For instance, the one between the O4D atom of the nitro group and the H atom linked to the methoxyl C10O atom, which is 2.625 Å, exits in the parallel adjacent molecules; meanwhile, the other from the O10 atom of the methoxyl group to the H atom attached to the phenyl C6H atom, which is 2.560 Å, is found in the almost perpendicular adjacent molecules. Additionally, intermolecular O—H···O hydrogen bonds are observed in the crystal structure of (**2**) (Table 3), which is not the case in (**1**). As a result, the two kinds of intermolecular interactions link the molecule into an infinite three-dimensional network (Fig. 5).

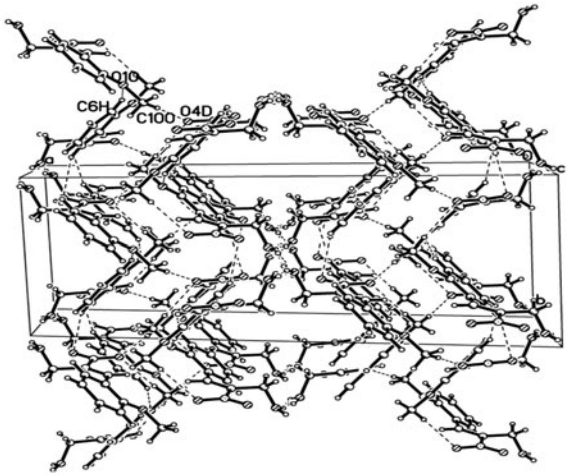


Figure 5. Crystal packing diagram of (**2**) along the *c*-axis.

Conclusions

In summary, two nitroalkene compounds [*trans*-2-(2-methoxyphenyl)-1-nitroethylene (**1**) and *trans*-1-hydroxymethyl-2-(2-methoxyphenyl)-1-nitroethylene dichloromethane hemisolvate (**2**)] have been synthesized and structurally characterized by elemental analysis and ^{1}H (^{13}C) NMR spectra. Particularly, the molecular structures of (**1**) and (**2**) were unequivocally determined by single-crystal X-ray diffraction analysis, where the C═C double bond is in a *trans* configuration in the solid state. In addition, the C─H···O short contacts exist in the crystal structures of (**1**) and (**2**).

Acknowledgments

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References

[1] Luo, M., & Yan, B. (2010). *Tetrahedron Lett.*, *51*, 5577.

[2] Rana, S., Mallick, S., & Parida, K. M. (2011). *Ind. Eng. Chem. Res.*, *50*, 2055.

[3] Louis-Ferdinand, R. T., & Fuller, G. C. (1970). *Toxicol. Appl. Pharmacol.*, *16*, 668.

[4] Latif, N., Mishriky, N., Girgis N. S., & Arnos, S. (1980). *Indian J. Chem.*, *19B*, 301.

[5] Canoira, L., Gonzalo-Rodriguez, J. G., Subirats, J. B., Escario, J. A., Jimenez, I., & Martinez-Fernandez, A. R. (1989). *Eur. J. Med. Chem.*, *24*, 39.

[6] Milhazes, N., Calheiros, R., Marquez, M. P. M., Garrido, J., Cordeiro, M. N. D. S., Rodrigues, C., Quinteira, S., Novais, C., Peixe, L., & Borges, F. (2006). *Bioorg. Med. Chem.*, *14*, 4078.

[7] Mohan, R., Rastogi, N., Namboothiri, I. N. N., Mobin, S. M., & Panda, D. (2006). *Bioorg. Med. Chem.*, *14*, 8073.

[8] Cheng, P., Jiang, Z. Y., Wang, R. R., Zhang, X. M., Wang, Q., Zheng, Y. T., Zhou, J., & Chen, J. J. (2007). *Bioorg. Med. Chem. Lett.*, *17*, 4476.

[9] Sheldrick, G. M. (1996). *SADABS: Program for Empirical Absorption Correction of Aera Detector Data*, University of Göttingen: Göttingen.

[10] Sheldrick, G. M. (1997). *SHELXS-97: Program for Crystal Structure Solution*, University of Göttingen: Göttingen.

[11] Sheldrick, G. M. (1997). *SHELXL-97: Program for Crystal Structure Refinement*, University of Göttingen: Göttingen.

[12] Cameron, T. S., Cowley, D. J., & Thompson, J. E. (1974). *J. Chem. Soc. Perkin Trans. II.*, 774.

[13] Pedireddi, V. R., Sarmab, J. P., & Desiraju, G. R. (1992). *J. Chem. Soc. Perkin Trans. II.*, 311.

[14] Nesterov, V. N., Kislyi, V. P., Timofeeva, T. V., Antipin, M. Y., & Semenov, V. V. (2000). *Acta Crystallogr.*, *C56*, e107.

[15] Xu, H., Sun, H. S., & Xu, N. (2009). *Acta Crystallogr.*, *E65*, o1691.

[16] Jing, L. H. (2009). *Acta Crystallogr.*, *E65*, o2521.

[17] Jing, L. H. (2009). *Acta Crystallogr.*, *E65*, o2809.

[18] Kennedy, A. R., Kipkorir, Z. R., Muhanji, C. I., & Okoth, M. O. (2010). *Acta Crystallogr.*, *E66*, o2984.

[19] Ren, Y. H., & Zhu, R. T. (2010). *Acta Crystallogr.*, *E66*, o2249.

[20] Zhao, P. H., Feng, Z. H., Zhang, M., Liu, Y. Q., & Zhao, G. Z. (2011). *Acta Crystallogr.*, *E67*, o3505.

[21] Zhao, P. H., Hao, E. J., Liu, Y. Q., & Zhao, G. Z. (2012). *Acta Crystallogr.*, *E68*, o1742.

[22] Radulović, N. S., Bogdanović, G. A., Blagojević, P. D., Dekić, V. S., & Vukićević, R. D. (2011). *J. Chem. Crystallogr.*, *41*, 545.

[23] Dewar, M. J. S., & Thiel, W. (1977). *J. Am. Chem. Soc.*, *99*, 4907.